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Steam Oxidation of FeCrAl and SiC in the Severe Accident Test Station (SATS)

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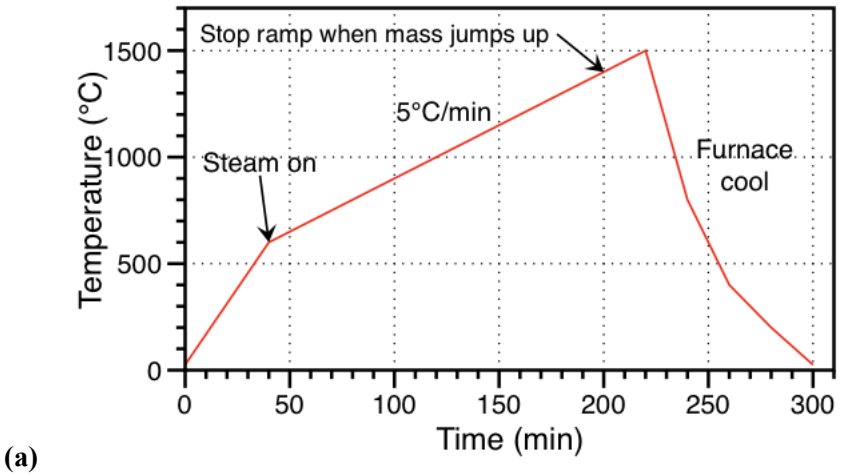
Introduction

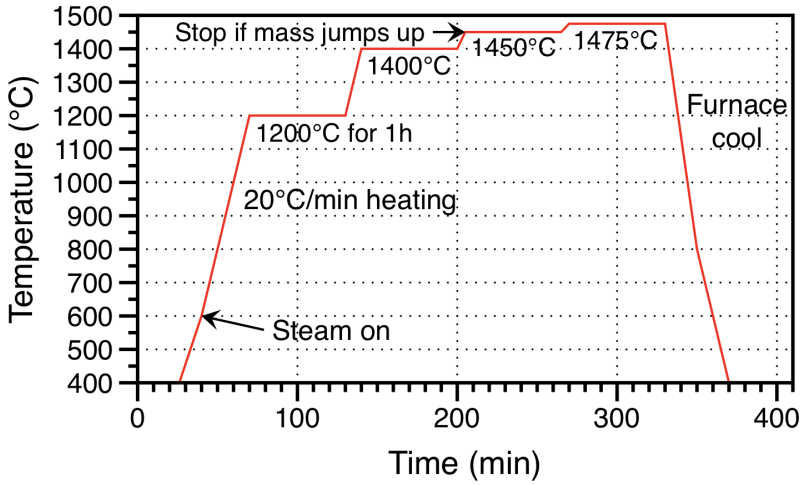
Numerous research projects are directed towards developing accident tolerant fuel (ATF) concepts that will enhance safety margins in light water reactors (LWR) during severe accident scenarios. In the U.S. program, the high temperature steam oxidation performance of ATF solutions has been evaluated in the Severe Accident Test Station (SATS) at Oak Ridge National Laboratory (ORNL) since 2012 [1-3] and this facility continues to support those efforts in the ATF community. Compared to the current UO_2/Zr-based alloy fuel system, alternative cladding materials can offer slower oxidation kinetics and a smaller enthalpy of oxidation that can significantly reduce the rate of heat and hydrogen generation in the core during a coolant-limited severe accident [4-5]. Thus, steam oxidation behavior is a key aspect of the evaluation of ATF concepts. This report summarizes recent work to measure steam oxidation kinetics of FeCrAl and SiC specimens in the SATS.

FeCrAl alloys

The first phase of evaluations of Fe-Cr-Al alloys examined the behavior of commercial and model alloys at Al content from 3-5% and Cr contents of 10-20% in steam at 1200°C [3]. However, more recently, a wider range of compositions has been evaluated with Al contents up to 8%. Also, there is more interest in identifying the maximum use temperature where the alloys can still form a protective alumina scale. Conventional FeCrAl alloys with ~20%Cr and 5%Al (e.g. Kanthal alloy APMT and cast FeCrAlY) can form alumina at 1475°C for 4h in steam. However, the high Cr content is a concern for α' embrittlement under irradiation [4-5]. Alloy development of lower Cr content FeCrAl has shown these alloys often have an issue forming alumina at ≥1400°C [6]. With the large range of compositions being evaluated, a rapid screening test was required to evaluate the steam oxidation behavior of these new compositions. Figure 1a shows the temperature profile of the ramp test that was used in the thermal gravimetric analysis (TGA) rig of the SATS to screen each of the new 1st and 2nd generation FeCrAl alloys. (The 1st generation alloys are ternary FeCrAl alloys with <0.1Y additions and the 2nd generation alloys contain additions such as Mo and Si to improve the mechanical properties [7].) The specimens are heated in argon to 600°C where the steam is introduced. The specimens are then heated to 1500°C at 5°C/min while the mass change is monitored. If the mass gain rises sharply past ~10 mg (>2 mg/cm^2) of mass gain, then the experiment is stopped and the specimen cooled to room temperature. The temperature where the specimen exceeded 2 mg/cm^2 is recorded as the maximum temperature (T_{max}) where a protective alumina scale could be formed. Figure 2 summarizes the T_{max} results of the new 1st and 2nd generation FeCrAl alloys. As noted in Figure 2a, the standard FeCrAl alloys with ~20Cr and ~5Al (e.g. Kanthal APMT) can complete the ramp test to 1500°C and maintain an alumina scale. Basic high temperature

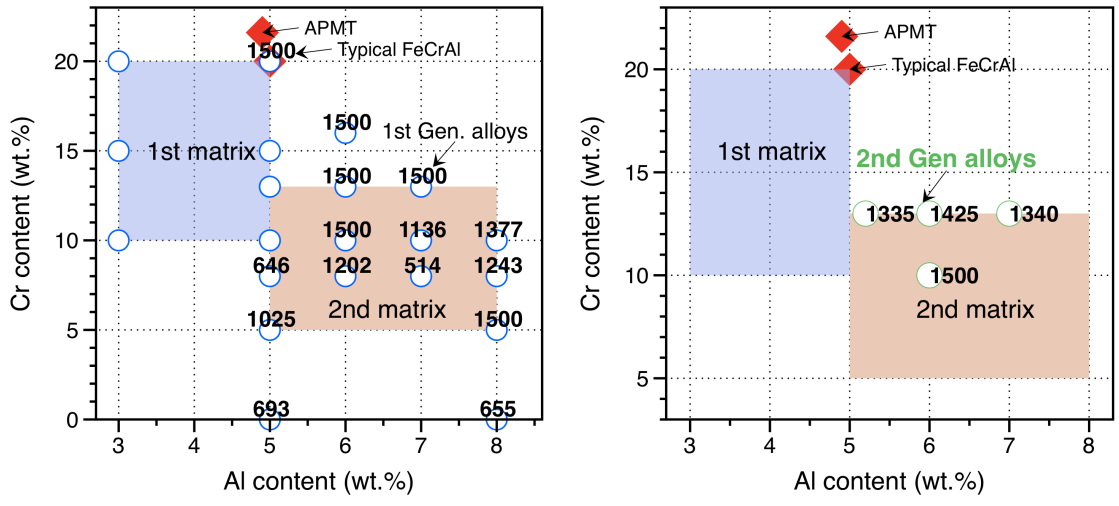


(a)



(b)

Figure 1. Temperature profile of the (a) "ramp" and (b) "step" tests in the SATS TGA module.



(a) (b)

Figure 2. Ramp test maximum temperature listed for various (a) 1st generation and (b) 2nd generation FeCrAl alloys.

oxidation understanding would suggest that higher Cr and Al contents would facilitate the formation of alumina and lead to higher T_{max} values. Figure 2 indicates several 6% Al alloys were able to form alumina to 1500°C but no clear correlations with Cr or Al contents are evident and in some cases the trends are opposite to expectations.

To follow up on the ramp test results, 4h isothermal experiments were conducted in the high temperature (HiT) furnace in the SATS, where the mass change is not continually monitored and the steam velocities are higher. These were the first types of experiments conducted on alloy APMT, which showed protective behavior in 1 bar steam at 1475°C in both the TGA and HiT SATS modules. Table 1 shows that many of the 6%Al alloys that performed well in the ramp test were not able to form a protective alumina scale after 4h at 1400°C in steam and were completely consumed as indicated by the very high mass gains (>100mg/cm^2) and the specimens completely consumed to oxide. Surprisingly, the only new alloy specimen that survived in these experiments was Fe-10Cr-8Al-Y, which had a T_{max} value of 1377°C. These contradictory results require further study but generally suggest that these alloys are all on the borderline of protective behavior under these extreme conditions. One hypothesis is that minor alloy defects, not present in all specimens, affect performance in these experiments and that multiple specimens need to be evaluated once the target alloy composition is narrowed.

One general question is about the role of steam on the observed oxidation behavior. To study the role of steam, several specimens have been exposed in the HiT furnace in flowing air for 4h at 1400°C. Table 1 summarizes the mass change for these materials and most of the alloys show low mass losses because the alumina scale spalled, presumably during cooling due to the strain caused by the thermal expansion mismatch between the alloy and the relatively thick alumina scale. Similar spallation was not observed for the Fe-20Cr-5Al alloy used as a baseline. If some type of oxide cracking occurs at temperature in steam, the disruption of the alumina layer could lead to accelerated oxidation as was observed in the steam tests for most of these alloys. The specimen of Fe-13Cr-7Al did not survive the 1400°C air oxidation exposure but did

Table 1. High temperature oxidation results for various 1st generation (B) and 2nd generation (C) FeCrAl alloys.

Alloy	1400°C air (mg/cm^2)	1400°C steam (mg/cm^2)	Ramp test T_{max} (°C)	Step test (mg/cm^2)
B 20Cr 5Al	1.5	1.4	1500	–
B 10Cr 6Al	-1.5	158	1500	0.2
B 10Cr 7Al	–	–	1136	1.1
B 10Cr 8Al	–	1.6	1377	1.8
B 13Cr 6Al	-0.5	164	1500	–
B 13Cr 7Al	117	148	1500	–
B 16Cr 6Al	-0.6	149	1500	–
C 10Cr 6Al	–	62	1500	1.7
C 13Cr 6Al	–	139	1425	1.4

perform well in the ramp test supporting an alloy defect hypothesis.

A second hypothesis about these results is that the ramp test is essentially pre-oxidizing the specimen by slowly heating to high temperature and allowing a protective alumina scale to form at lower temperatures before the specimen reaches the highest temperatures, Figure 1a. In contrast, the specimens were heated to 1400°C in the HiT furnace in argon and then steam was introduced at the start of the 4h hold (similarly air was only introduced at 1400°C for the 4h air exposures). For these lean alloys, there is an extreme change in environment at the start of the isothermal experiments from argon to an H_2O oxidant, which is obviously more aggressive than O_2 (i.e. air) based on the results in Table 1. To test this hypothesis, a second TGA test was developed, called the "step" test where the specimen is pre-oxidized in steam for 1h at 1200°C and the specimen is heated to 1200°C similar to all isothermal tests in the TGA, Figure 1b. After 1h at 1200°C, the specimen is heated to 1400°C for 1h, then 1450° and finally to 1475°C for 1h. By conducting the test in the TGA, if the specimen shows rapid oxidation, the experiment can be stopped before the specimen is consumed. Table 1 shows the final mass gain results (after cooling to room temperature) for the specimens exposed in the experiments. All of the specimens tested to date have survived the "step" exposure to 1475°C. Therefore, the "pre-oxidation" effect likely explains some of the differences observed between the isothermal and ramp testing. These results also indicate that the isothermal experiments in steam may be too aggressive to evaluate the leaner FeCrAl alloys. In an actual accident scenario, the ramp test is a more realistic assessment of alloy performance. In the future, multiple ramp tests may be performed on an alloy to determine reproducibility. As noted by the missing data in Table 1, some experiments have not been performed yet or are in progress.

Silicon carbide composite specimens

The main testing performed for the ATF community in FY15 has been steam oxidation testing of SiC composite specimens for Westinghouse. Ten experiments were performed, typically for 48h at 1300° or 1500°C in the TGA module of the SATS in 1 bar steam. Figure 3 shows some of those results. These experiments were much longer than the 4h experiments typically performed in the TGA. Compared to prior results for relatively pure CVD (chemical vapor deposition) SiC [8], the mass gains were relatively large for some of these composite specimens and can be attributed to additives (e.g. sintering aids) in these specimens affecting the high temperature oxidation. Large oxide bubbles were evident on all of the specimens exposed at 1500°C.

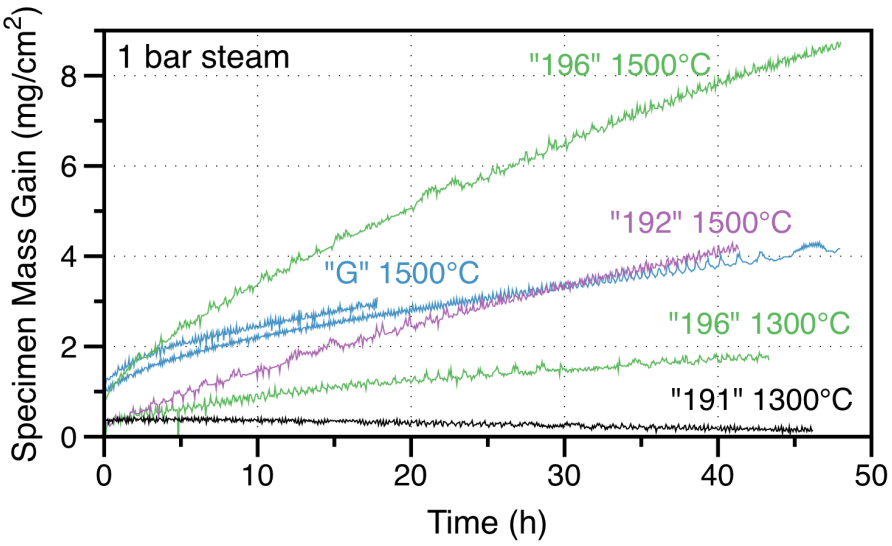


Figure 3. Mass change of various SiC composite specimens in 1 bar steam.

Summary

Over the past several years, the high temperature steam oxidation resistance of many different alternative fuel cladding materials has been evaluated in the ORNL SATS. The main focus for the past year has been low-Cr FeCrAl compositions. Two different high temperature screening tests, the "ramp" and "step" tests, have been developed to assess their maximum use temperature compared to conventional FeCrAl alloys. Some inconsistencies in steam oxidation behavior have been noted but a better understanding is developing of the role of steam and experimental conditions in the oxidation of these new compositions at up to 1500°C. In particular, exposing bare metal specimens to high temperatures is not recommended and either slowly heating to high (≥1400°C) temperature or pre-oxidizing at lower temperature is recommended. As the composition range for a commercial FeCrAl tube is narrowed, more focused experiments will continue to further understand the high temperature oxidation behavior.

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